INFRARED PROPERTIES OF 40-60 MEV ELECTRON-IRRADIATED GERMANIUM*

UNPUBLISHED PRELIMINARY DATA

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The use of infrared absorptivity to study and characterize on a microscopic scale the radiation-induced defects in silicon has proved to be an important probe.[1-7] In previous studies by other experimenters the defects were produced by low energy electrons[1-6] ($E \lesssim 4.5$ Mev), deuterons[1] (9.6 Mev) and reactor neutron irradiation.[1,4,5,7] The first reported results on the use of infrared techniques in the study of irradiated germanium was recently given by R. Whan.[9,10] In Whan's experiments 2 Mev electrons and reactor neutrons were used to produce defect infrared active bands.

We shall report on the annealing of defect infrared bands induced by 40-60 Mev electrons in low oxygen containing ($\lesssim 10^{16} cm^{-3}$) and high oxygen containing ($\gtrsim 10^{17} cm^{-3}$) single crystal germanium.* The sample temperature was kept at $T \lesssim 40^{\circ}C$ during irradiation. The electrons were incident on the sample in a $\langle 111 \rangle$ direction which also served as the direction of the infrared beam during spectrum measurements.

The characteristics of the germanium samples studied together with the incident electron energy, resistivity values before and after irradiation, total integrated fluxes and sample thicknesses are given in Table I.

The annealing experiments were performed in an electric furnace using silicone oil as the heat transfer medium for anneals up to 290°C. For anneals above 300°C, air served as the heat transfer medium. Sample temperature during anneal was controlled to ± 1°C

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*Obtained from Semi-Elements, Inc., Saxonburg, Pennsylvania.

in the oil bath and controlled to ± 3°C when air was used as the heat transfer medium. The infrared spectrometer settings were kept the same during each spectrum run after anneal in order to simplify comparison of the various spectra and allow relative measurements of defect concentration (area under absorption peak) to be made easily.

In Fig. 1 are shown the infrared spectra in the region 600-900 cm^{-1} of sample #7.2 n-type germanium (oxygen concentration[11] before irradiation 1.2 x $10^{17} cm^{-3}$) after various twenty minute anneals at the temperatures indicated. The spectra were measured with the sample temperature kept at 80°K. The spectrum measured after the 410°C anneal exhibits no radiation-induced defect absorption bands. The 11.7 micron band is characteristic of atomically dispersed oxygen in germanium.[11] From Fig. 1 it can be seen that at least twelve new vibrational bands in the 600-900 cm^{-1} region (11.1-16.7 μ wavelength region) are produced by the irradiation. These bands are associated with oxygen-defect complexes since 1) after irradiation we found a marked decrease in the intensity of the 11.7 micron (860 cm^{-1})band and 2) bands* in the region 10-16 microns do not appear after irradiation of low-oxygen containing germanium samples #5.2 and #6.2. After irradiation of the p-type germanium sample (#5.2) we observed no new defect absorption bands but only a 15-20% general reduction in

*Both n-type germanium samples #6.2 and #7.2 which are converted to p-type by the irradiation exhibit infrared spectra in the 2 to 8 micron region which are characteristic of unirradiated p-type germanium. (See H. B. Briggs and R. C. Fletcher, Phys. Rev., 87, 1130 (1952) and W. Kaiser, R. J. Collins, and H. Y. Fan, ibid, 91, 1380 (1953).)

transmission over the wavelength region 2 to 8 microns. Upon annealing to temperatures in the range 150-280^{o}C, the infrared transmission properties from 2 to 8 microns of all samples returned to their pre-irradiation values.

The growth and decay of the more prominent bands in Fig.1 can be more easily followed by presenting the isochronal annealing results as plots of relative defect concentration vs. annealing temperature. Shown in Figs.2 and 3 are isochronal annealing results on the more prominent bands presented in Fig.1 in the region 618 to 875 cm^{-1}. In Figs.2 and 3 one can see a striking growth of defect bands at 717, 729, 768, 753, 794 cm^{-1} after annealing the 618 and 724 cm^{-1} bands. The annealing behavior of these oxygen-vibrational bands is rather similar to results obtained by others(4,5,6) in the irradiation of oxygen-containing silicon. A comparison of our results (Fig.1) to reactor neutron irradiated oxygen-containing germanium by Whan(9,10) shows that neutron irradiated germanium gave rise to four bands 710, 726, 768, 774 which correspond to the 717, 724, and 729, 768, and 775 cm^{-1} bands which we give in Fig.1. The additional bands which we resolve were not observed by Whan which we believe is due to the fact that Whan(9) used samples only one mm thick and measured the infrared spectrum at room temperature.

From an irradiation at -180^{o}C Whan(10) concluded that oxygen vibrational defect bands at 710, 726, 768, and 774 cm^{-1} do not originate from primary defects, rather, they originate from defect complexes formed at temperatures where the primary defects are mobile. This conclusion was reached by Whan since the defect bands appeared only after warmup to 50°C. Additional evidence for this conclusion is evident in Figs.1, 2 and 3 in which it is apparent that these bands grow and decay as the 618 cm^{-1} band anneals. The results in Figs.1 and 2 strongly suggest that analogous to the case of oxygen-doped silicon,[2,6] the band at 618 cm^{-1} may be the "germanium A center" comprising a single oxygen atom attached to a vacancy. The frequency ratio of the 618 cm^{-1} defect band relative to the 855 cm^{-1} oxygen band of germanium is in the same ratio as the 834 cm^{-1} defect band (silicon A-center) to the 1103 cm^{-1} oxygen band of silicon. Moreover, the 618 cm^{-1} band is the first to anneal in germanium which is also similar to the case of silicon in which it is found that the "A-center" disappears first upon heat treatment.[6,12]

The isochronal annealing results on the prominent bands shown in Figs.2 and 3 indicate that there are at least four annealing temperature ranges at $T \sim 160°C$, $T \sim 220°C$, $T \sim 320°C$ and $T \sim 400°C$. In contrast Whan[9] reports only two temperature ranges from her annealing experiments.

It is possible that the four annealing temperature ranges correspond to different configurations of single and multiple vacancies coupled to oxygen atoms. Analogous results have been obtained for the case of 1.4 Mev[6] and 40 Mev[12] electron irradiation of oxygen-containing silicon. However, it is reasonable to expect that the 40 Mev irradiation produces a higher concentration of divacancies, etc., than the 1.4 Mev electron irradiation. In order to examine this point further, we shall perform electrical and infrared property measurements on irradiated oxygen doped germanium.

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LIST OF REFERENCES

1. H. Y. Fan and A. K. Ramdas, J. Appl. Phys., 30, 1127 (1959).
2. J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev., 121, 1015 (1961).
3. G. D. Watkins, J. W. Corbett and R. S. McDonald, Bull. Am. Phys. Soc., 5, 26, (1960).
4. H. Y. Fan and A. K. Ramdas, Proc. of the Int'l. Conf. on Semiconductor Physics, Prague (1960) p.309.
5. A. K. Ramdas and H. Y. Fan, Jour. Phys. Soc., Japan, 18, Supp. II, 33, (1963).
6. J. W. Corbett, G. D. Watkins, and R. S. McDonald, Phys. Rev., 135, (5A) 1381, (1964).
7. M. Balkanski and W. Nazarewicz, Jour. Phys. Soc., Japan, 18, Supp. II, 37, (1963).
8. G. D. Watkins, and J. W. Corbett, Phys. Rev., 121, 1001, (1961).
9. R. E. Whan, and H. J. Stein, Appl. Phys. Letters, 3, 187 (1963).
10. R. E. Whan, Bull. Am. Phys. Soc., 9, 278, (1964).
11. W. Kaiser, J. Phys. Chem. Solids, 23, 255, (1962).
12. J. C. Corelli, G. C. Oehler, J. F. Becker and K. J. Eisentrant, to be published in the J. Appl. Phys. (May 1965).

TABLE I

Sample Characteristics, Incident Electron Energy, Resistivity Values, Total Integrated Flux and Thickness of Samples Studied.

Sample No.	Type and Impurity	Resistivity* Before Irradiation (ohm-cm)	Resistivity* After Irradiation (ohm-cm)	Crystal Growing Method	Incident Energy (Mev)	Total Integrated Flux e/cm^2	Thickness (mm)
5.2	p-type Ge Indium	0.1	0.351	Pulled	36	5.6×10^{18}	4.24
6.2	n-type Ge Antimony++	0.14	0.342	Pulled	36	2.8×10^{18}	4.34
7.2	n-type Ge++ Oxygen	1.0	0.570	Pulled**	57	3.3×10^{18}	[illegible]

* Pre-irradiation value @ $300^{\circ}K$.

** Grown in a partial atmosphere of oxygen.

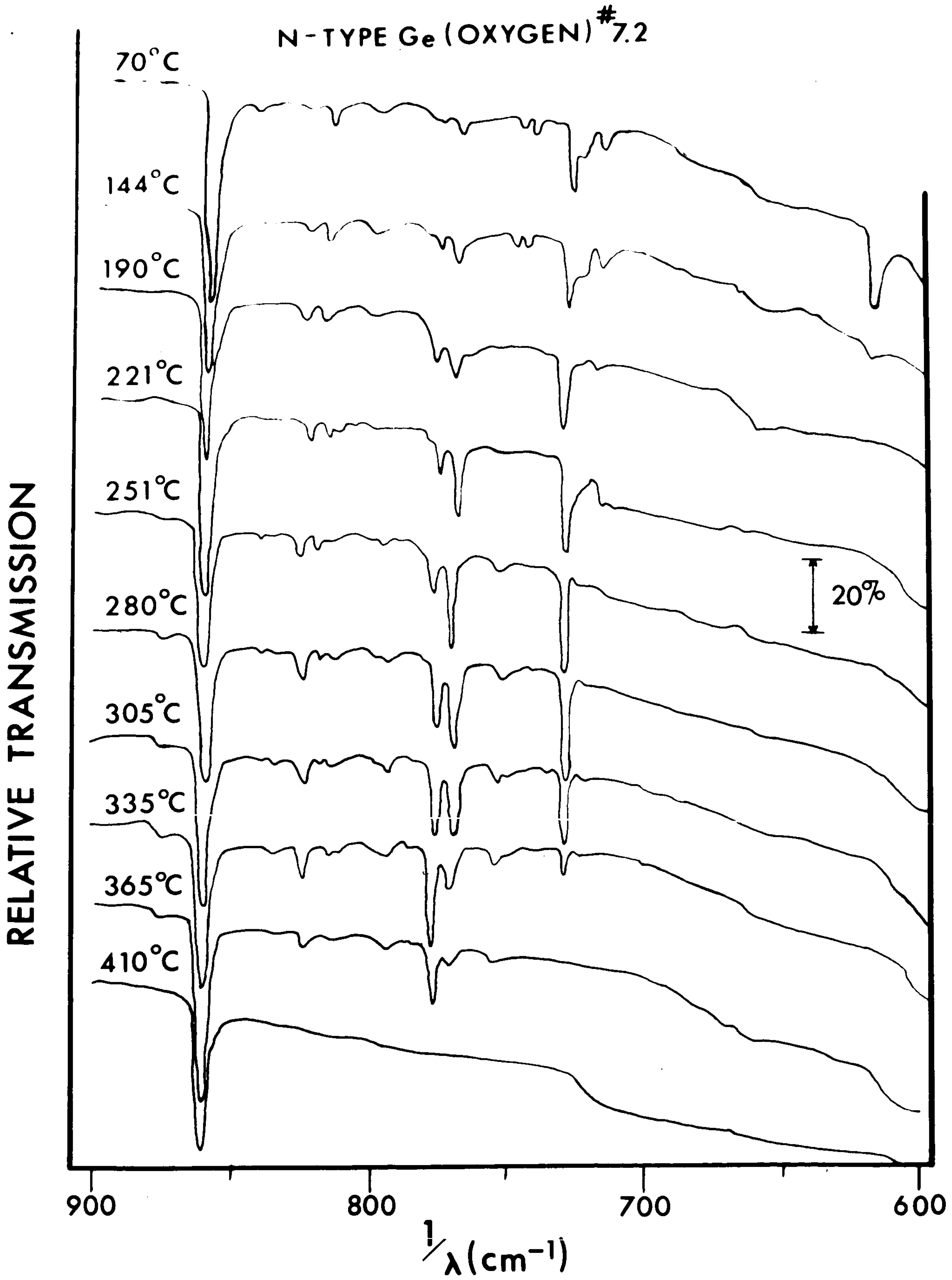
++ p-type after irradiation.

LIST OF FIGURE CAPTIONS

Fig. 1 Infrared absorption spectra of oxygen-containing germanium (sample #7.2) in the region 618 cm^{-1} to 880 cm^{-1} measured at $80^{o}K$ after various anneals at the temperatures shown. See Table I for sample details.

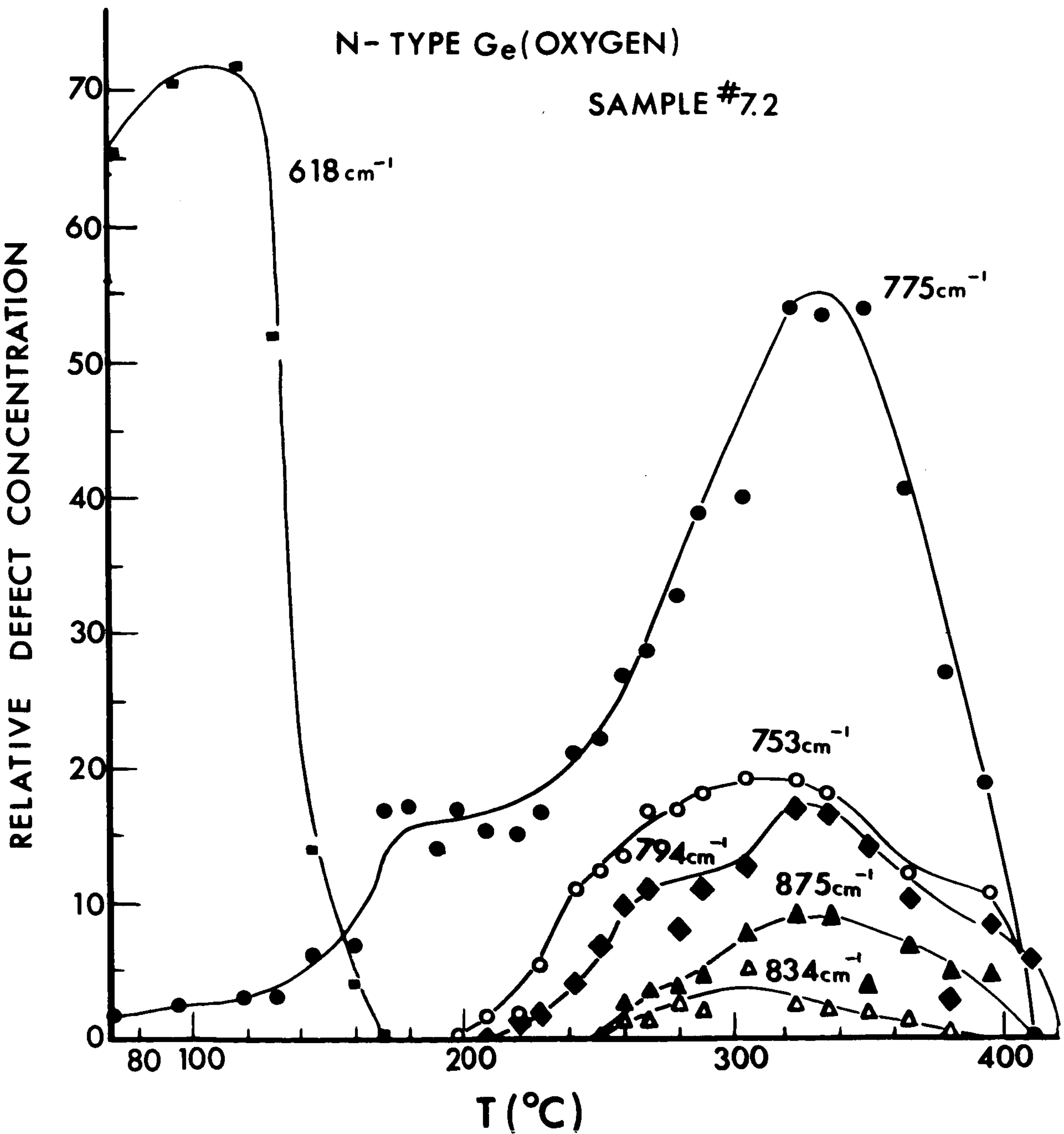
Fig. 2 Isochronal annealing of radiation-induced oxygen-defect lattice vibrational bands (in the range 618 cm^{-1} to 834 cm^{-1}) vs. annealing temperature for oxygen containing germanium (sample #7.2). All measurements were made at $80^{o}K$. See Table I for sample details.

Fig. 3 Isochronal annealing of radiation-induced oxygen-defect lattice vibrational bands in the range 729 cm^{-1} to 813 cm^{-1} vs. annealing temperature for oxygen containing germanium (sample #7.2). All measurements were made with sample at $80^{o}K$. See Table I for sample details.



N-TYPE Ge (OXYGEN) #7.2
70°C
144°C
190°C
221°C
251°C
280°C
305°C
335°C
365°C
410°C
20%
RELATIVE TRANSMISSION
900
800
700
600
1/λ (cm⁻¹)

Figure 1



N- TYPE Ge(OXYGEN)
SAMPLE #7.2
618cm⁻¹
775cm⁻¹
753cm⁻¹
794cm⁻¹
875cm⁻¹
834cm⁻¹
RELATIVE DEFECT CONCENTRATION
0
10
20
30
40
50
60
70
80
100
200
300
400
T(°C)

Figure 2

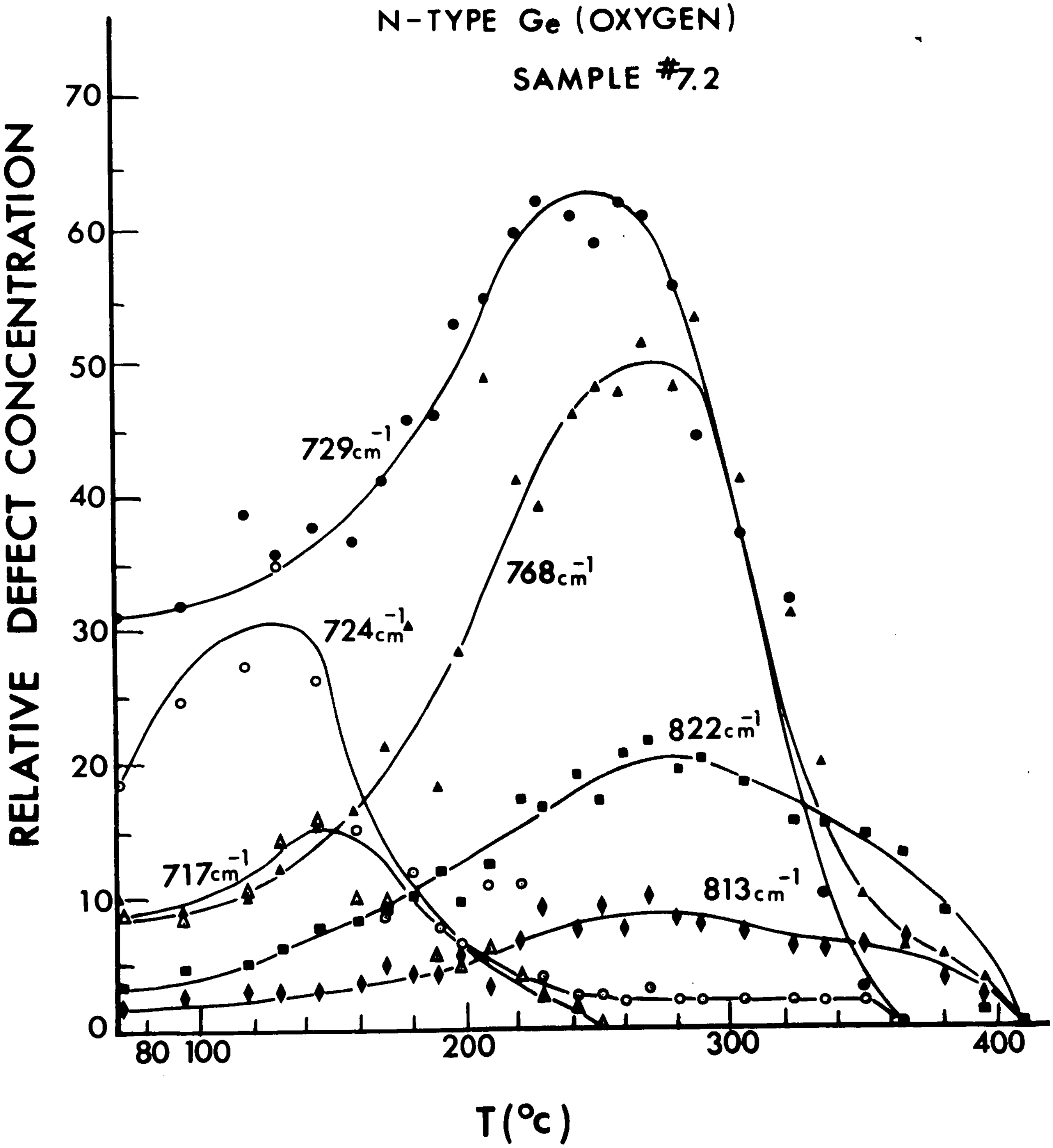

N-TYPE Ge (OXYGEN)
SAMPLE #7.2
RELATIVE DEFECT CONCENTRATION
70
60
50
40
30
20
10
0
729cm-1
768cm-1
724cm-1
822cm-1
717cm-1
813cm-1
80
100
200
300
400
T(°c)

Figure 3